Development of alkali free glaze for refractory application

A THESIS SUBMITTED IN THE PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE DEGREE OF

BACHELOR OF TECHNOLOGY

IN

CERAMIC ENGINEERING

BY

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CERTIFICATE

This is to certify that the thesis entitled, "**Development of Alkali-free glaze for refractory application**" submitted by **Mr. Sai Shankar Pradhan** (Roll no. 110CR0631) in partial fulfillment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela. It is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

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ACKNOWLWDGEMENT

The satisfaction that accompanies the successful completion of any task is incomplete without mentioning the people who made it possible through their constant guidance and support and encouragement that crowns all the efforts with success.

It gives me immense pleasure to express my utmost respect and deepest gratitude to my guide, **Dr. Sumit Kumar Pal**, for his esteemed guidance, innovative thinking, functional freedom and encouragement showered on me.

I would also like to thank all the professors, especially **Dr. Ritwik Sarkar**, for their valuable suggestions and encouragements at various stages of the work.

I am thankful to all the staff members and research scholars who have always helped me and guided me in getting various works accomplished. My most sincere gratitude to **Mr. Ezhil Venuswaran** for constantly being there for my help and help me their way best in this project.

Lastly I am thankful to my parents and friends, for their love and support throughout the project.

Thanking you,

Sai Shankar Pradhan

ABSTRACT

In the high temperature applications, mostly in the molten metal casting industries, the carbonaceous refractory bricks had been widely used due to its better thermal shock resistance and well appreciated mechanical properties. In most of the cases, the major problem had been faced due to the low oxidation resistance of the carbonaceous refractory bricks. In spite of the addition of the antioxidant, the level of oxidation had been the major problem faced by the Ceramic Engineers. In this scenario, an alkali free glaze composition had been developed, which can be applied as an antioxidant coating on the refractory bricks. $Al_2O_3 - SiO_2 - B_2O_3 - MgO - CaO$ Glass system had been taken for the preparation of glaze. The glaze maturing temperatures had been determined by firing the glaze samples at 1350°C, 1450°C and 1500°C. Four glaze compositions had been prepared and applied on the zirconia-graphite refractory bricks. After glaze application, the bricks had been tested for oxidation. Brazilian disc test had been done for the glaze samples to determine the tensile strength. Rheological properties of the glaze compositions had been analyzed by using the Rheometer. Phase analysis of the oxidized and fired glaze samples had been done by powder X-ray diffraction method. Furthermore the FTIR analysis of the glass powder had been done for the identification of different bonds present. Vickers hardness of the annealed glass samples had been done.

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CHAPTER 1

INTRODUCTION

1.1 GENERAL INTRODUCTION

In the white ware industry, glazing is considered to be an interesting phenomenon due to its peculiar characterization. The main objective of glazes in the white ware industry is to provide coatings, which has different requirements with respect to the application. Some glazes are applied to generate some colors on the ceramic bodies. Few glazes are used to provide 0% porous coating on the ceramic bodies. This is mainly done to arrest the penetration of dust, water and other foreign particles to the ceramic bodies. Apart from the white ware industry, refractory industries also seek the utility of glazes for wide range of applications.

Inclusion of carbon in the refractory bricks had pronounced well with better mechanical properties and thermal shock resistance. Zirconia- graphite, Magnesia-Carbon and Alumina – Carbon are commercially used carbonaceous refractories. Carbonaceous refractories are generally used in submerged pouring nozzles, ladle to tundish and shroud tubes. The above mentioned accessories are developed and used in the continuous metal casting systems. The elemental carbon present in the carbonaceous refractory bricks, often exist in the form of flake graphite, which serves to protect the refractory from physical attack and erosion by molten metals.

1.2 CONTINOUS METAL CASTING SYSTEM

The entire the molten metal casting system is constructed by using the carbonaceous refractories. According to the operating temperatures and viscosity of the molten metal, the selection of refractories had been carried out. The Fig1.1 shows the complete layout of the continuous metal casting system.

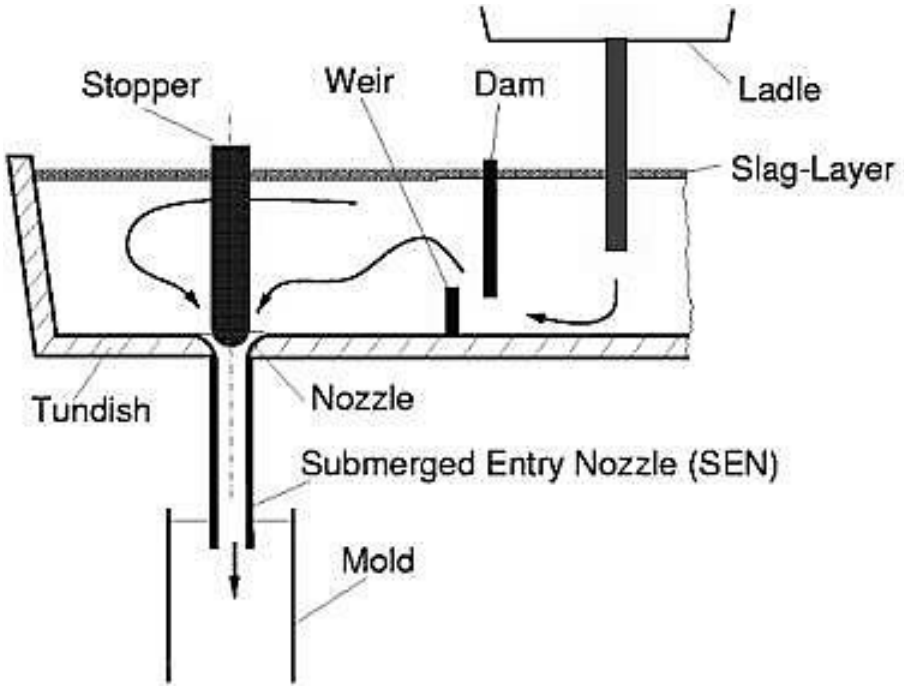

Fig 1.1 – Schematic representation of the continuous metal casting system

The outer layer of the system is constructed by metal panels and inner lining of each module had been constructed by using carbonaceous refractories. The ladle acts as a reservoir which provides the molten metal and the inlet of the molten metal had been navigated by a sliding gate of the ladle. The orientation of the molten metal had been mention clearly in the Fig 1.1. Weir and dam take care of the molten flow into the submerged entry nozzle. Due to low density of the slag, the molten slag will be pushed up by the molten metal and had been collected by the slag layer.

In this casting process, the biggest problem lies in the oxidation of carbon. Elemental carbon is susceptible to air oxidation at temperatures above 600^0C. The level of oxidation has to be minimized during preheating and casting operations, for a better life of the refractory bricks. A major oxidation protection has to be provided to the submerged entry nozzle (SEN), which will create impurities or oxidized phase in the casted body if the protection fails.

In this case, 2—3 hours of preheating and up to 5 hours of casting time is observed at a temperature of about 1400°C. Some preventive measures have to be undertaken to restrict the level of oxidation during this period.

1.3 ROLE OF ANTIOXIDANT IN CARBONACEOUS REFRACTORIES

Elemental carbon in refractories is oxidized in two ways: direct oxidation and indirect oxidation. Direct oxidation occurs under 1400^0C (reaction-1), when carbon is oxidized directly by the oxygen from atmosphere. Indirect oxidation occurs above 1400^0C where carbon is oxidized by the molten slag (reaction-2).

$$2C_{(s)} + O_{2(g)} \xrightarrow{<1400^\circ C} 2CO_{(g)} \qquad \ldots\ldots\ldots\ldots\ldots (1)$$

$$C_{(s)} + FeO_{(l)} \xrightarrow{>1400^\circ C} Fe_{(l)} + CO_{(g)} \ldots\ldots\ldots\ldots\ldots (2)$$

In this scenario, to reduce the level of oxidation or loss of carbon, antioxidant coatings are provided on the surface of the carbonaceous refractory bricks. Al, Si, SiC, B_4C are commonly used antioxidants in carbon based refractories. Among them Al metal powder is prominently used as an antioxidant in most of the refractories. But addition of antioxidant directly to the refractory bricks creates a problem later. Initially it acts a protective layer for the refractory brick. Later on, the antioxidant will get oxidized and forms a ceramic layer which further acts as a protective layer. But due to change in volume and differential shrinkage, after oxidation, most of the refractive bricks got cracked and creep had been developed. Thus the overall refractory properties had been detoriate.

1.4 NECESSITY OF GLAZE LAYER COATING

In order to overcome this problem, in the current work, it had been decided that a glaze layer will be developed on the surface of the refractory brick, which not only acts as protective layer for the refractory brick but also acts as an anti-oxidant layer.

Several parameters have to be evaluated and many factors have to be taken into consideration for the application of glaze layer on the carbonaceous refractory bricks.

- The melting point of the glaze should be more than the operating temperatures of molten metal casting furnaces. The glaze should be optimized with high viscosity on the operating temperatures.
- High differential shrinkage / expansion at higher temperatures lead to formation of weak interface between the glaze layer and the refractory brick. In order to avoid this thermal mismatch, similar thermal expansion should be there between glaze and bricks.
- In order to avoid the low melting phases, alkali oxides should be removed from the glass system, since the presence of alkali oxides acts as a flux.

In order to obtain a higher temperature of glaze maturing, alkali free glass can be used in the glaze composition. Moreover the alkali free glaze composition possesses high viscosity at high operating temperatures, which favours better protection for the refractory bricks. The application of the glaze on the refractory should achieve zero surface porosity in the operating temperatures. The viscosity of the glaze has to be optimized in order to satisfy the above mentioned criteria. This optimization is purely depends on the glaze composition and the rheology of the glaze slurry during application. The processing technique for the glaze composition also plays a key role in order to achieve zero surface porosity.

1.5 PROCESSING TECHNIQUES OF GLAZE LAYER COATING

The application of glaze layer on the carbonaceous refractories can be carried by any one of the following processing techniques:

1. Dip coating
2. Flood coating
3. Electrostatic spray coating
4. Brushing
5. Sputtering

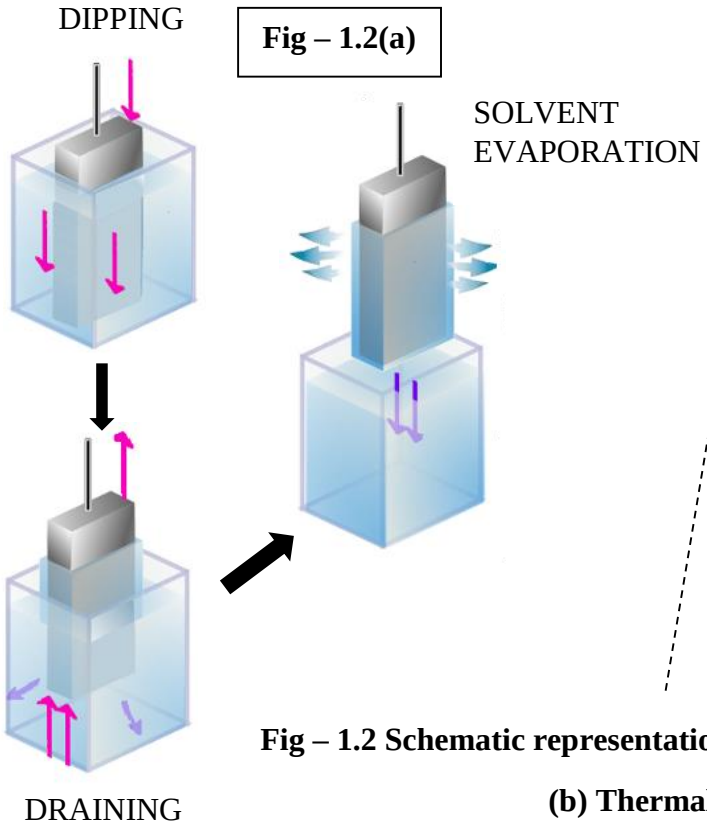

Fig – 1.2(a)

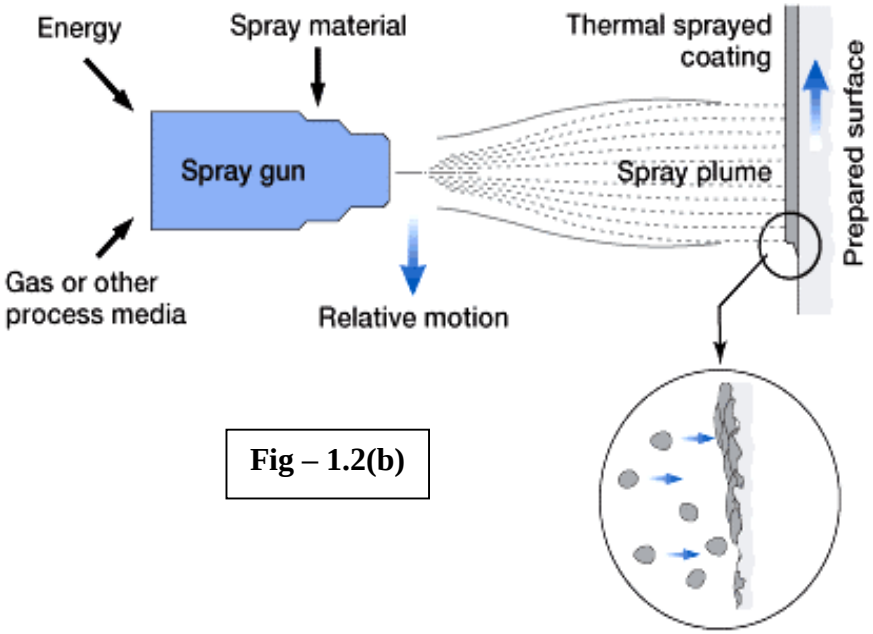

Fig – 1.2(b)

Fig – 1.2 Schematic representation of coating process (a) Dip coating method (b) Thermally activated spray coating method

According to the thickness of the glaze layer required, the selection of processing technique has to be carried out. The rheology of the glaze slurry prepared has to be optimized according to the requirement of the glaze properties. Each processing technique of glaze coating features with distinct properties. In short, the selection of processing technique has to be done when the rheology of the glaze slurry is fully optimized. The Fig 1.2 and 1.3 illustrates the schematic representation of the dip coating and thermally activated spray coating process respectively.

1.6 GLAZE MATURING TEMPERATURE

Before starting the application of glaze on the refractory, an important parameter which has to be analyzed, is the glaze maturity. During heat treatment, the rate of increase in temperature significantly influences the melting activity. Long firing schedule will ensure better inter particle interaction on the glaze layer. In case, if the firing schedule is restricted with insufficient time, then the particles with low melting points in the glaze composition will become viscous very early. In this scenario, the particles with high melting point will be remained unreacted with the viscous flow of the low melting phases. In short, after firing, it can be observed that the former possess a well-developed glaze regions than the latter. The half melted or un-melted regions of the glaze layer increase the surface porosity. This will be the serious problem and the intention of utilizing the glaze layer will be badly interrupted. A good protective glaze layer never exposes the refractory surface or creates surface porosity, which leads to the penetration of molten metal to strike the refractory surface. Thus by correlating the rheology of glaze composition, this glaze maturing temperature plays a vital role.

1.7 OBJECTIVE OF THE CURRENT WORK

To achieve better life span and to prevent oxidation of the carbonaceous refractory bricks, it had been decided that development of an alkali free glaze layer on the refractory bricks will serve the purpose. The outline of the current work had been illustrated below:

- Preparation of an alkali free glass frit for glaze composition to avoid formation of low melting phases in the glaze at operating temperatures.
- FTIR analysis of the alkali free glass powder
- Vickers hardness testing of the annealed alkali free glass samples
- Preparation of Glaze compositions by varying the amount of ball clay and antioxidant
- Determination of glaze maturing temperatures
- Study of the rheological properties of the glaze composition
- Application of glaze slurry on the zirconia-graphite refractory brick by the method of brushing
- Oxidation test of glaze coated zirconia-graphite refractory bricks
- Phase analysis of the glaze on the operating temperatures

CHAPTER 2

LITERACTURE REVIEW

2.1 ELEMENTAL CARBON AND GLAZE IN REFRACTORIES

Inclusion of carbon in the refractories had created a good impact in the mechanical properties and prevention of oxidation. Additional to that, these carbon elements acts as lubricating agent which completely avoid the penetration of molten metal into the refractories. Furthermore, these carbon elements have high thermal conductivity which actually regulates heat throughout the molten chamber. In spite of these merits, the level of oxidation on the refractories creates a question mark for the life span of them. To avoid this situation, these carbonaceous refractories demands for a protective layer which should be capable of arresting the oxidation process and increase the life span of the refractories. Addition of antioxidants had contributed some good results but still the life span of the refractories had been retained the same as before. In this scenario, use of glaze as a protective layer had been expected to be as a solution for the current problem.

2.2 FORMULATING GLAZE COMPOSITION

Antioxidant is considered to be one of the prime additives in the glaze composition. Si, Al and B_4C are commonly used antioxidant for the restriction of carbon oxidation. Borosilicate glass frits are preferably included to acquire a softening point below 600^0C, which will favor better viscosity at high operating temperatures. Ball clay is predominantly used as a binder in the glaze composition which withstands at a temperature of glaze maturity.

Buchanan et al [4], clearly visualized the role of an inhibitor, which was added up to 2 wt.% along with the glaze composition. An inhibitor performs the following function along with glaze in the operating temperatures:

1. Restriction of hydrogen molecule evolution from the aqueous glaze slip
2. It stabilizes the glaze at operating temperatures
3. Bubbles had been removed from the glaze compositions after application on the refractory surface
4. It supports the formation even coating

The inhibitors suitable for this application are maleic anhydride, succinic acid, poly-acrylic acid, boric acid, sodium metasilicate, sodium dihydrogen phosphate, sodium triphosphate and Zinc chloride [4].

The glass frit composition has to be formulated in such a way that it should attain high viscosity to avoid the flow off from the refractory surface. Research had been done for the application of glaze on the outer surface of the refractory to prevent oxidation of graphite [3]. The necessary components of the glaze had been illustrated in the table 2.1.

Table 2.1 – Glaze components and its quantity [3]

S.No:	Glaze components	Quantity (in wt.%)
1.	Glass frits	40-80
2.	Antioxidant	2-30
3.	Inhibitor	< 2
4.	Refractory filler	< 20
5.	Binder	0-20
6.	Optional additives	< 10

2.3 SELECTION OF GLASS SYSTEM FOR GLAZE

Buchanan et al had selected SiO_2 - B_2O_3 - Na_2O - P_2O_5 as their glass system for the formulation of glaze. In this case, B_2O_3 acts as a modifier, which creates the low melting phase of the glass. Al_2O_3, CaO, MgO, Bi_2O_3 and ZrO are the other modifiers used for the preparation of glass frits. Each combination of glass system modifies the overall glaze maturing temperature. The main objective of the formulation of glass system is to attain high viscosity at operating temperatures. Keeping that in mind, **Buchanan et al** tried with different glass composition as shown in the table 2.2.

Table 2.2 – Different glass system used for the application of glaze on refractories [4]

Component	**Glass A (wt.%)**	**Glass B (wt.%)**	**Glass C (wt.%)**	**Glass D (wt.%)**	**Glass E (wt.%)**	**Glass F (wt.%)**
SiO_2	31.43	27.41	59.32	33.55	-	35.0
B_2O_3	30.62	31.29	21.58	16.55	8.18	20.0
P_2O_5	-	-	-	-	40.92	-
Li_2O	-	-	-	0.99	4.23	-
Na_2O	21.07	19.45	10.69	-	22.61	10.0
K_2O	4.64	3.75	2.45	-	-	-
Al_2O_3	7.56	13.84	5.12	7.27	24.06	10.0
Bi_2O_3	-	-	-	41.64	-	-
CaO	3.45	3.16	0.65	-	-	19.0
MgO	0.54	0.39	0.19	-	-	-
ZrO	0.69	0.71	-	-	-	6.0

2.4 IMPORTANCE OF ALKALI FREE GLASSES IN GLAZE APPLICATIONS

`Alkali free glasses are more desirable for refractory glazes as the formation of low melting phases can be avoided. Recently, Alkali free glass compositions are widely used in the thin film applications [9]. Prominently these alkali free glasses are used in thin film transistors, Liquid display crystal screen and Plasma assisted liquid crystal display. Selections of these alkali free glasses in these applications are due to its high thermal shock resistance, high tensile strength and good chemical durability. In the presence of an alkali metal oxide in the glass system, the alkali metal ions are diffuse into the thin film, whereby the film properties are likely to deteriorate. In the case of glazes on refractories, the above mentioned properties are well appreciated. Different combinations of alkali free glasses had been tried by **Ulrich Peuchert et al** and had been reported (ref [9], page 7, 8).

On a different perspective, better results with thin layers of glaze coatings are most welcomed in the refractory applications. As a conclusion from the above mentioned literature, it had been decided that an alkali free glass composition will fetch better results on the glaze composition.

2.5. PROCESSING TECHNIQUES OF GLAZE APPLICATION

Rancuolle et al [3] proposed a method for applying a coating of fused silica slurry on alumina-graphite refractory. The refractory body is preferably glazed and kept at ambient temperature for open air drying or preheated to a temperature of about 70°C-l20°C. The solid loading of the fused silica slurry is about 70-85 wt. %. Immersion time, rheology of slurry and preheating or drying schedule are the important factors taken into consideration.

Table 2.3 – Coating thickness vs. immersion time on corresponding preheating temperature by the dip coating method [3].

Preheating temperature (in °C)	**Coating thickness (in mm)**	**Immersion time (in seconds)**
100	2	10
100	2.5-3.5	20
100	4-5	30
60	N/A	10
60	1.0	20
60	2.0	30

Buchanan [4] had stated that, the coating may be applied to the composition by dip coating, flood coating, spray coating, and electrostatic spray coating or brushing. It will be appreciated by those who are skilled in the art, since the aqueous glaze slip composition may optionally include additives such as a suspension agent, a hardener, a binder and/or a surfactant. According to the principle of the coating method, the optional additives, either inorganic or organic, will be included into the glaze slurry. The schematic representation of dip coating and thermally activated spray coating had been mentioned in the Fig – 1.2.

2.6. EFFECT OF ANTIOXIDANTS

A.S. Gokce et al [5] studied the effect of different antioxidants on magnesia carbon refractory brick. Al, Si, Mg, B_4C are the antioxidants used in their investigation. Evaluation of carbon losses had been the prime objective of their study. On addition of B_4C, magnesium borate is the compound formed on the operating temperature.

This is to be noted that those magnesium borate phases were in liquid state at 1360°C, which filled up the open pores presented in the refractories. Spinel formation had been observed when Si and Al metal powders are added as an antioxidant in the MgO-C refractory. At an operating temperature of about 1500°C (for 6hours), it had been noticed that 3 wt. % antioxidant addition shown distinguishable carbon losses. About 70, 50, 35 and 20wt. % of carbon losses had been shown by the antioxidants SiC, Si, Al and B_4C respectively. Without addition of antioxidant, around 90 wt. % of carbon losses had been observed.

2.7 CONCLUSIONS FROM THE LITERACTURE

From the above mentioned literatures, it had been clearly shown that formulation of alkali free glass frits will provide better oxidation resistance and high viscosity to the glaze composition. Furthermore, addition of antioxidants along with the glaze enriches the prevention of oxidation. In this scenario, optimization of the rheology of the glaze slurry will play a major role in the thickness of the glaze layer.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 ALKALI FREE GLASS SYSTEM AND RAW MATERIALS

As discussed in the literature, for the application of glaze on carbonaceous refractory bricks, alkali free glass system has to be formulated. The alkali free glass system had been formulated and illustrated in the table 3.1.

Table 3.1- Alkali free glass composition

GLASS COMPONENTS	SiO_2	Al_2O_3	B_2O_3	MgO	CaO
WEIGHT %	57.9	16.1	11.1	4.4	10.6
RAW MATERIALS	Fused Silica	A-17 Alumina	Boric Acid	Magnesia	Calcium Carbonate

In this composition, silica will acts as a network former. CaO and MgO stabilize the glass melts at high temperature. Alumina is included to perform as a glass forming agent. Addition of Boron trioxide will help the melt to control at higher temperatures. Furthermore the Boron trioxide acts as a flux and performs the role of an alkali oxide.

3.1.1 PREPARATION OF ANNEALED GLASS AND GLASS FRITS

As per the batch calculation, the above mentioned raw materials are mixed homogenously and filled up in the sillimanite crucible. The batch had been melted at 1550°C, at a heating rate of about 5°C/min. After soaking the melt at 1550°C for a period of 2 hours, the melt had been quenched in water for the formation of glass frits. With the similar melting schedule, another batch of raw materials had been melted and poured in graphite plate for annealing. The annealing had been done at a temperature of about 600°C, in an electric heater for a period of one hour and cooled at open atmosphere.

3.1.2 FORMATION OF GLASS POWDER

The water quenched glass frits are wet milled (water media) in a planetary milling machine for a period of 6 hours at 350 rpm, in a silicon nitride milling jars. Then wet milled slurry had been dried at 100°C, in Dry air Owen for 12 hours. Then the dried glass powder had been taken for sieve analysis for the determination of average particle size. The final powder had attained a particle size of about 20 µm.

3.1.3 FTIR ANALYSIS OF GLASS POWDER

The FTIR analysis of the glass was done to determine the bonds present in the glass system using FTIR spectroscopy, "Model: Alpha –E, Company: Bruker" machine. This analysis had been done in reflectance mode and the resulting spectra had been plotted between Reflectance (R) vs. wave number (cm^{-1}) by using Origin Pro-8 software.

3.1.4 VICKERS HARDNESS OF THE ANNEALED GLASS

The hardness of the annealed glass had been determined by undergoing Vickers Hardness Test, by using Vickers Indentation Tester – LV 700. Micro indentation had been given to the annealed glass samples at a load of 0.5kgf. The indentation tip of the tester is in the shape of a rhombus and so the indented area will be in the shape of a rhombus. The indented surface is clearly visualized by an optical microscope and the lengths of the diagonals are measured. Then hardness had been determined by using the formula,

$$\text{Vickers Hardness, } Hv = (1.8544*p)/d^2,$$

Where p is applied load and d is the average length of the diagonals (mm).

3.2 FORMATION OF GLAZE COMPOSTION

In this current work, four different glaze compositions had been prepared as illustrated in the table-3.2.

Table 3.2 – Illustration of Glaze compositions

COMPONENTS	**COMPOSITION 1 (in wt.%)**	**COMPOSITION 2 (in wt.%)**	**COMPOSITION 3 (in wt.%)**	**COMPOSITION 4 (in wt.%)**
Glass powder (20µm)	59	59	49	49
Ball Clay (30 µm)	10	20	10	10
Aluminum Powder (25µm)	30	20	40	30
Boric Acid	1	1	1	1
Fused Silica (15 µm)	0	0	0	10

In the above mentioned compositions, aluminum metal powder acts as an antioxidant. Ball clay is used as a binder as well plasticizer. Fused silica will perform the functions of refractory filler. During operating temperatures, boric acid will be decomposed into Boron trioxide and fulfills the functions of an inhibitor.

3.2.1 ANALYSIS OF GLAZE MATURITY

As discussed in the section 1.6, glaze maturity is the prime objective of this current work. A 1g batch of glaze compositions had been mixed well in a mortar and pestle. The mixed powder had been compacted into a pellet by using die punch of 15mm diameter, at 6ton pressure, on a uniaxial pressing machine. These pellets had been fired at 1350°C, 1450°C and 1500°C, which are considered as the operating temperatures of the glaze layer on refractory. After firing, if the pellets are found to have glassy phase with well-developed bonding, then it can be concluded that the glaze composition had attained its maturity.

3.2.2 BRAZILIAN DISC TEST FOR THE GLAZE SPECIMEN

With 1g batch of the glaze composition, pellets of 12mm diameter had been prepared by uniaxial pressing and fired at 1500^0C. The Brazilian disc test had been undergone with these fired glaze specimens on a uniaxial loading UTM. Then the circumferential tensile stress of the glaze specimen had been evaluated by using the formula,

$$\sigma_t = \frac{P_{max}}{\pi R t}$$

Where, σ_t is circumferential tensile stress, R - radius of the sample, t - thickness of the sample and P_{max} is the maximum peak load.

3.2.3 RHEOLOGY OF THE AQUEOUS GLAZE

Since the processing technique selected for the formation of glaze layer on the refractory is brushing, it is obvious that aqueous glaze has to be prepared. To have a better coating, rheology of the aqueous glaze has to be studied.

The aqueous glaze had been prepared by 30 wt. % of glaze composition dispersed in 70wt. % of water, which includes citric acid (5wt. %) solution, which had been used as a deffloculant. After preparation of the aqueous glaze, they had been transferred to the rotational Rheometer. The rotational Rheometer, (RheolabQC) works on the principle of Searle principle. The Rheometer rotates and measurement of shear rate and shear stress had been done on randomly selected 10 regions of rotating slurry. The obtained data had been plotted by shear rate vs. shear stress.

3.2.4 APPLICATION OF GLAZE ON REFRACTORY

The prepared aqueous glaze had been applied by the method of brushing. Zirconia-graphite refractory brick samples had been taken for the glaze application. The coating is done in such a way that refractory surface is never exposed. The thickness of the glaze layer provided is about 3mm. After the application of glaze on the refractory, the samples had been undergone open air drying for 2hours, followed by owen drying at a temperature of 50°C for 6hours. Then the glazed refractory bricks are fired at 1500°C, at a soaking time of 1 hour.

Fig 3.1 – Application of aqueous glaze on the zirconia-graphite refractory brick samples before drying

Fig 3.2 – Glazed zirconia-graphite refractory brick samples after drying

3.2.5 PHASE ANALYSIS OF GLAZE SPECIMENS

Glaze specimens which had been fired at 1500°C and 1550°C for 2 hours, are crushed into powder and phase analysis had been done by using X-ray diffraction method. This is to determine the phases formed after oxidation of the antioxidants. The X-ray diffraction data was recorded using X'pert Diffractometer at scanning range of 10^0-60^0 at step size of 10^0/min.

3.2.6 OXIDATION TEST OF THE GLAZED REFRACTORY SAMPLES

The glazed refractory bricks had undergone oxidation test, by firing the samples at 1500^0C and 1550^0C for 2 hours, in an electric furnace. After oxidation, the samples had been cut into slices for visualizing the glaze-refractory interface and level of oxidation.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. FTIR ANALYSIS OF ALKALI FREE GLASS POWDER

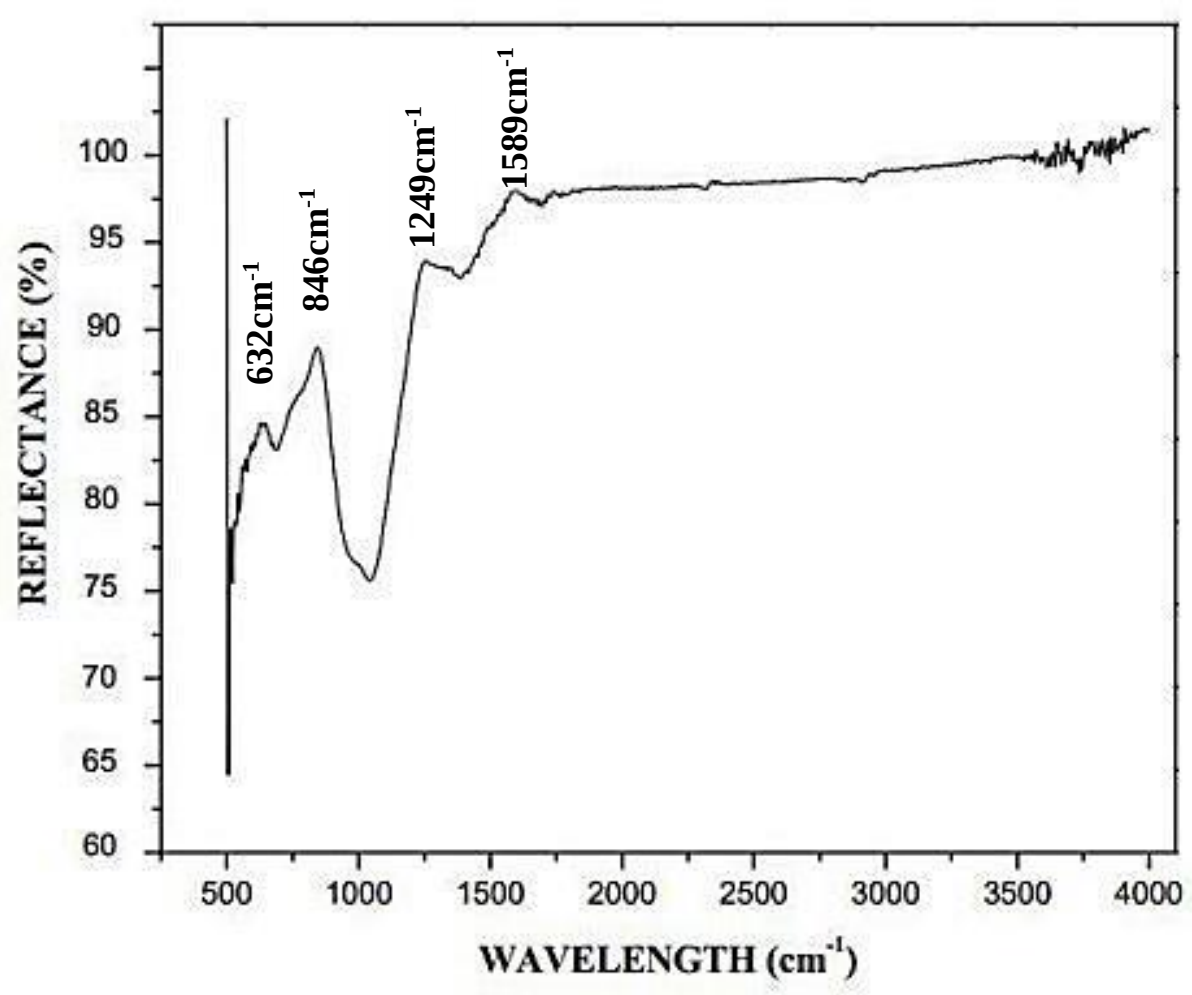

Fig- 4.1 FTIR Analysis of Alkali free glass powder – reflectance mode

The band from 500 to 540cm^{-1} is assigned to vibrations of Si-O bonds [13]. Thus, the faint vibrations of reflection of IR around 521 and 511cm^{-1} is attributed to the Si-O bonds. Absorption of IR below 690cm^{-1} is attributed to cationic vibrations in the network [14].

The band from 830 to 1109cm^{-1} assigned to stretching vibrations of Si–O–Si of [SiO_4] structural unit is overlapped by a band attributed to stretching vibrations of B–O– B of [BO_4].

Absorption bands in the range of 650–800 cm^{-1} is assigned to the formation of the AlO_4 structural units that behave as a network former [14]. 400 to 600cm^{-1} is assigned to the bending vibrations of the Al-O-Al of Al-O-Si bonds and the region between 691cm^{-1} to 720cm^{-1} is for the bending vibration of B-O-B in BO_3 triangles. The major peaks are observed at 637cm^{-1}, 841cm^{-1}, 1255cm^{-1} and 1584cm^{-1}. The minor and faint reflections below 690cm^{-1} are attributed to the cationic vibrations in the region.

The peak at 841cm^{-1} is assigned to Si-O-Si bonds of [SiO_4] structural unit. The absence of sharp peaks between 400 to 600cm^{-1} calls for the absence of Al-O-Al bonds. Similarly the absence of AlO_4 structural units can behave as network formers is indicated by the absence of troughs in the range of 650–800 cm^{-1}. The peak at 1255cm^{-1} is B–O stretching vibrations of triangular BO_3 units only. The peak at 1584cm^{-1} $B\text{-}O^-$ bond stretching in [BO_3] units due to varied groups.

4.2. VICKERS HARDNESS OF THE ANNEALED GLASS

The Vickers hardness test was conducted on the glass piece obtained from batch 2 by pouring the melt over a graphite plate. The Vickers hardness of the glass sample was conducted at 0.5kgf with 2s dwelling time. **The Vickers hardness value Hv of the glass was found to be 625.**

4.3. ANALYSIS OF GLAZE MATURITY

The glaze maturing temperature was found out in accordance with the method described earlier. The pellets were fired at 1350^0C, 1450^0C, and 1500^0C. No substantial glassy phase was found to be developed at the lower two temperatures. At 1500^0C, substantial glassy phase was found and the glaze seemed to be in its optimal state. At higher temperature, the glass frit had its melting point and was thus not considered optimum for glaze maturation.

Thus the glaze maturing temperature was fixed at 1500^0C.

The weight of the samples was noted before and after firing the glaze at the maturing temperature as given in the table – 4.1. A gain in weight was observed which was primarily due to the conversion of aluminum powder in the glaze into alumina due to oxidation and formation of liquid phase.

Table – 4.1 Weight of the glaze samples before firing and after firing

Composition	Initial weight (g)	Final weight (g)	Gain in weight (g)
1	1.881	1.993	0.112
2	1.922	1.961	0.039
3	1.739	2.034	0.295
4	2.039	2.169	0.13

From the above table it is clear that the gain in weight is maximum for composition 3 which has higher aluminum content compared to the other compositions. As a result, a higher gain in weight is observed due to more aluminum getting oxidized to alumina. Fig 4.2 and 4.3 represents the nature of the glaze samples before and firing respectively.

Fig 4.2 Photographic Image of the glaze samples before firing

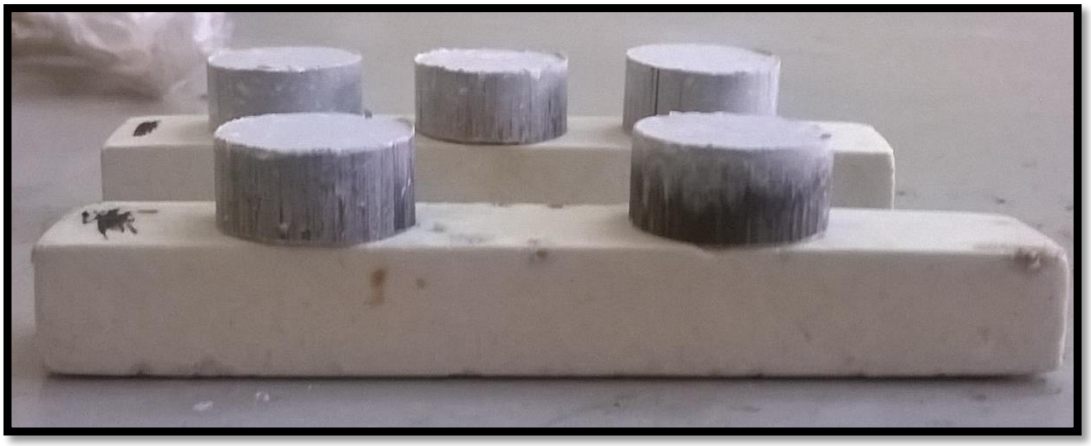

Fig 4.3 Photographic Image of the glaze samples after firing at glaze maturity temperature

4.4. BRAZILIAN DISC TEST RESULTS FOR THE GLAZE SPECIMEN

The Brazilian disc test was performed on the glaze samples according to the method described earlier. The table 4.2 shows the calculation of circumferential tensile stress of the glaze samples fired at 1500^0C and 1550^0C for 2 hours respectively.

Table 4.2- Brazilian Test results of glaze samples fired at 1500^0C and 1550^0C for 2 hours

Composition	Firing Temp. (°C)	R (mm)	T (mm)	Pmax (N)	σ_t (x10^7)
1	1500	7.4	7.08	2009	1.22
2	1500	7.26	6.46	2207	1.49
3	1500	6.84	6.30	2590	1.912
4	1500	7.18	6.46	2316	1.5887
1	1550	7.28	7.06	2015	1.274
2	1550	7.53	7.22	2123	1.242
3	1550	7.12	6.97	2625	1.683
4	1550	6.96	6.48	2719	1.918

4.5 RHEOLOGICAL BEHAVIOR OF AQUEOUS GLAZE

As discussed earlier, the flow property of the aqueous glaze plays a prominent role in the glazing on refractory bricks. It is necessary that the protective glaze layer on the refractory should cover fully with uniform coating. Thus the necessity for the analysis of rheological property of the aqueous glaze came into the picture. As per the protocol mentioned in the experimental section (ref 3.2.3), the acquired values from the Rheometer had been plotted (Fig 4.4).

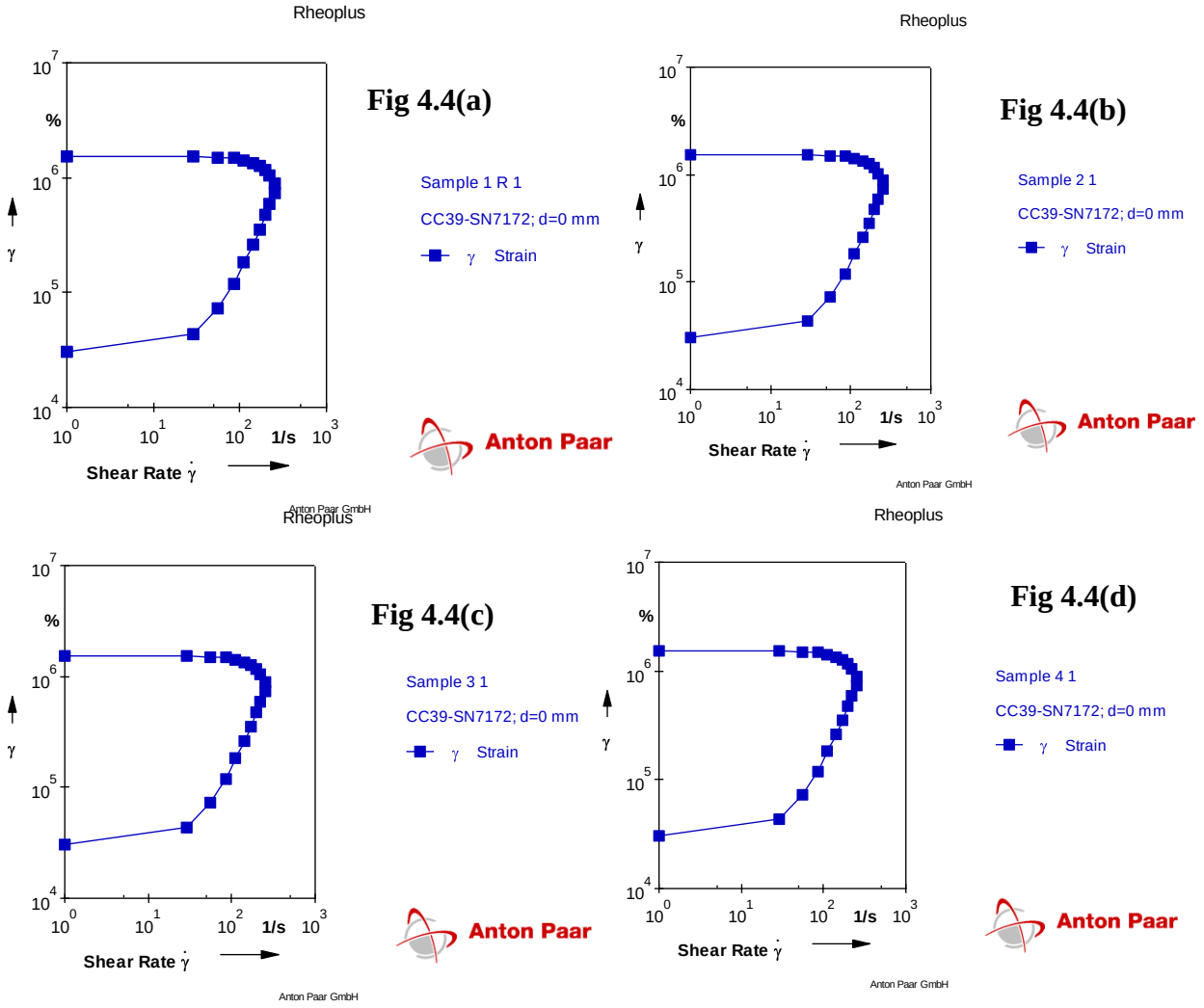

Fig 4.4 – Shear rate vs. Shear stress of the aqueous glaze

Fig 4.4(a), 4.4(b), 4.4(c) and 4.4(d) represent the rheological behavior of glaze compositions 1, 2, 3 and 4 respectively. The characteristic curve of shear stress vs. shear rate resembles the thixotropic behavior of the aqueous glaze. It is to be noted that viscosity of the aqueous glaze beyond this limit leads to the uneven coating of the glaze on the refractory bricks.

4.6 PHASE ANALYSIS RESULTS OF THE FIRED GLAZED SPECIMENS

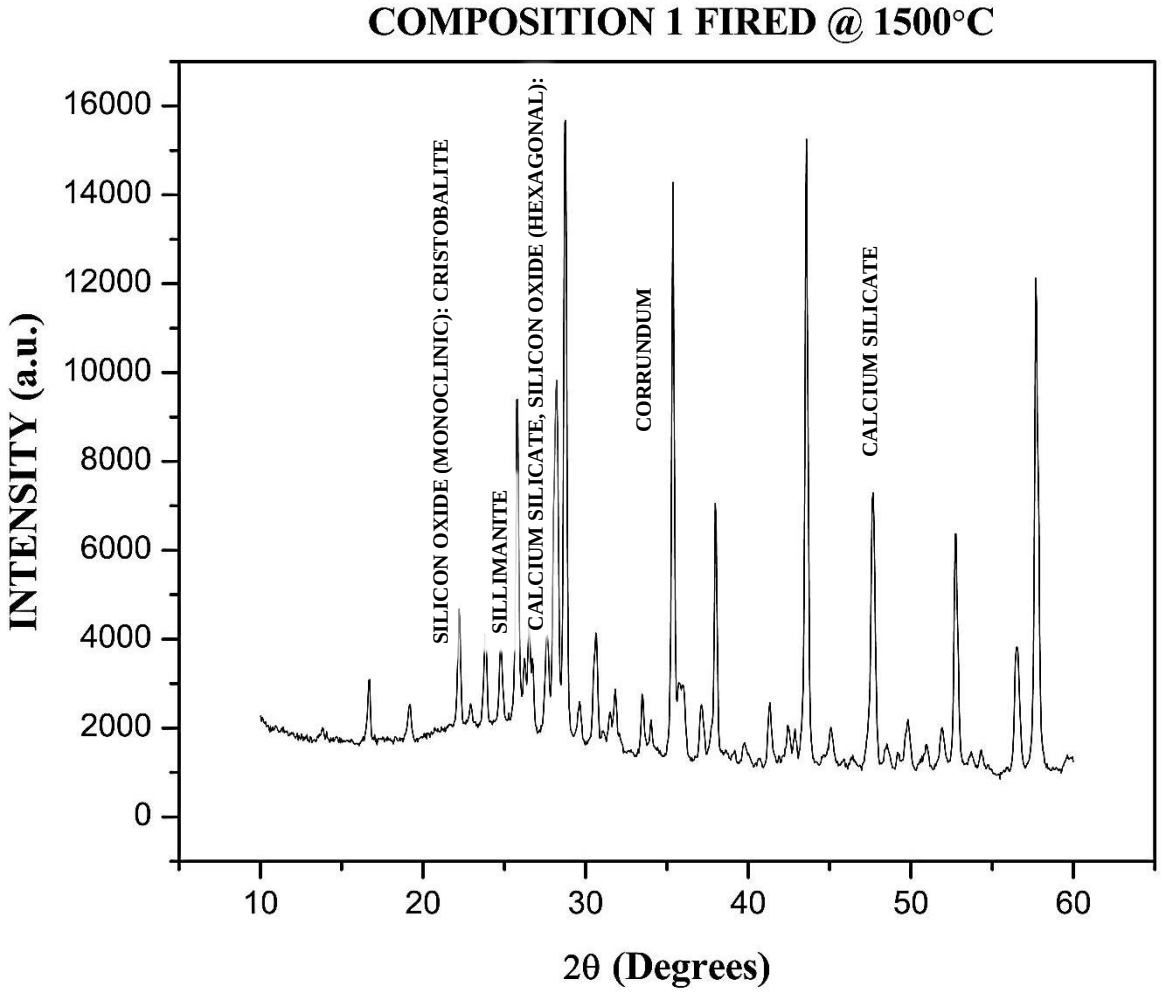

Fig 4.5 – Phase Analysis of glaze sample – composition 1 fired @ 1500°C/2hours

The Fig-4.5 shows the phase analysis of glaze composition 1 fired at 1500°C / 2 hours. The major phases formed were monoclinic silicon oxide, sillimanite, hexagonal silicon oxide, corundum and some silicates such as calcium silicate.

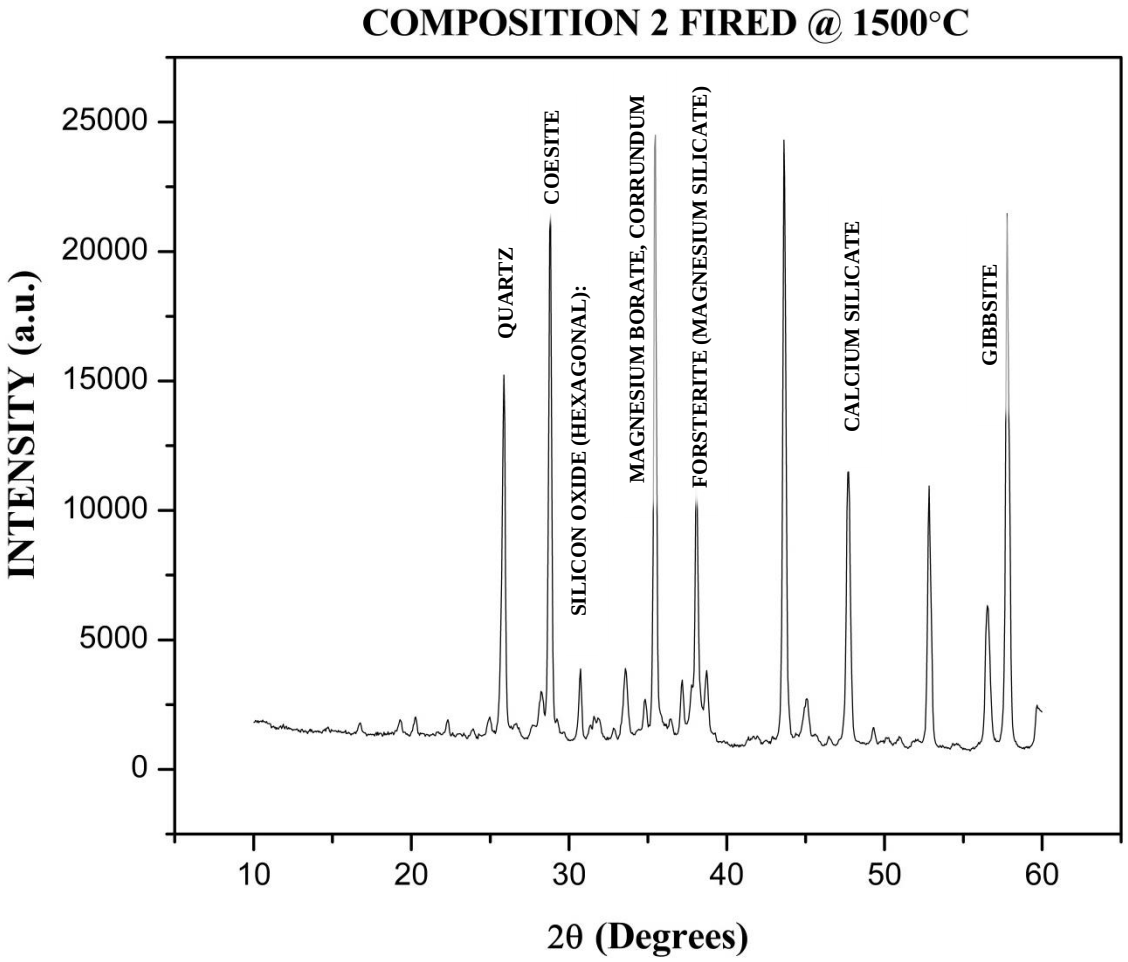

Fig 4.6 – Phase Analysis of glaze sample – composition 2 fired @ 1500°C/2hours

The Fig-4.6 shows the phase analysis of glaze composition 2 fired at 1500°C / 2 hours. The major phases formed were Quartz, hexagonal silicon oxide, silicon oxide in the form of coesite, aluminum oxide in the form of corundum, Magnesium borate, magnesium silicate (fosterite), and calcium silicate. Gibbsite was also found, probably due to the presence of ball clay which was added in the glaze composition.

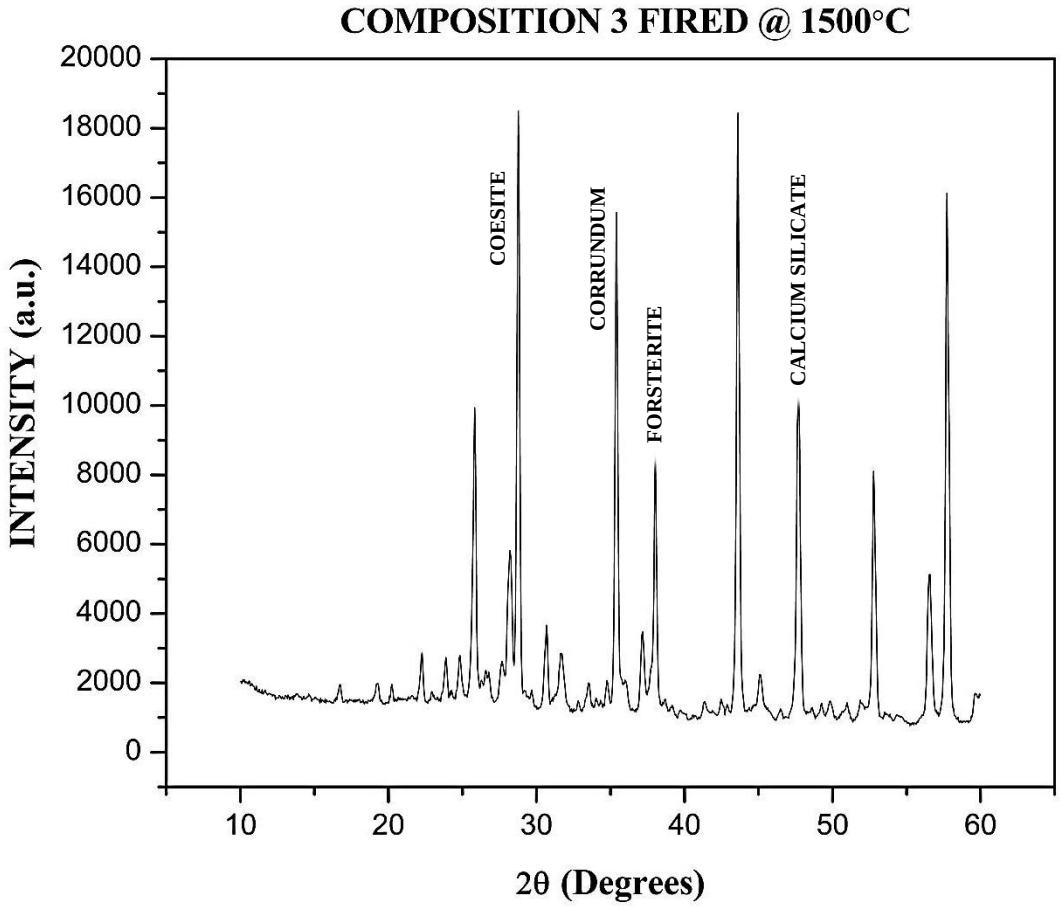

Fig 4.7 – Phase Analysis of glaze sample – composition 3 fired @ 1500°C/2hours

The Fig-4.7 shows the phase analysis of glaze composition 3 fired at 1500°C / 2 hours. The major phases were again similar to the previous one with oxidized aluminum in the form of corundum and Silica in the form of coesite, along with Calcium silicate and fosterite.

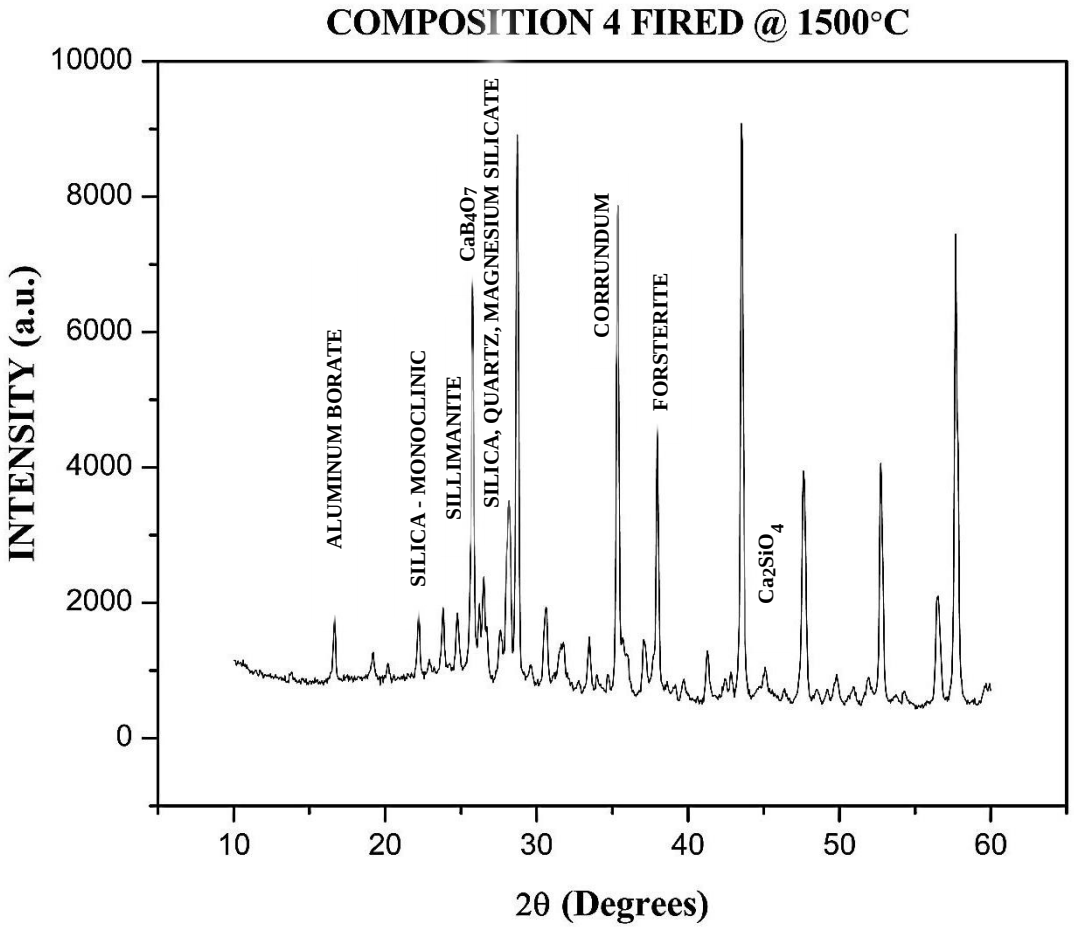

Fig 4.8 – Phase Analysis of glaze sample – composition 4 fired @ 1500°C/2hours

The Fig-4.8 shows the phase analysis of glaze composition 4 fired at 1500°C / 2 hours. The major phases found were monoclinic silica; silica in the form of coesite, silimanite was found in small amount, alumina in corundum, fosterite, calcium silicate, aluminum borate with Al-B-O bonding.

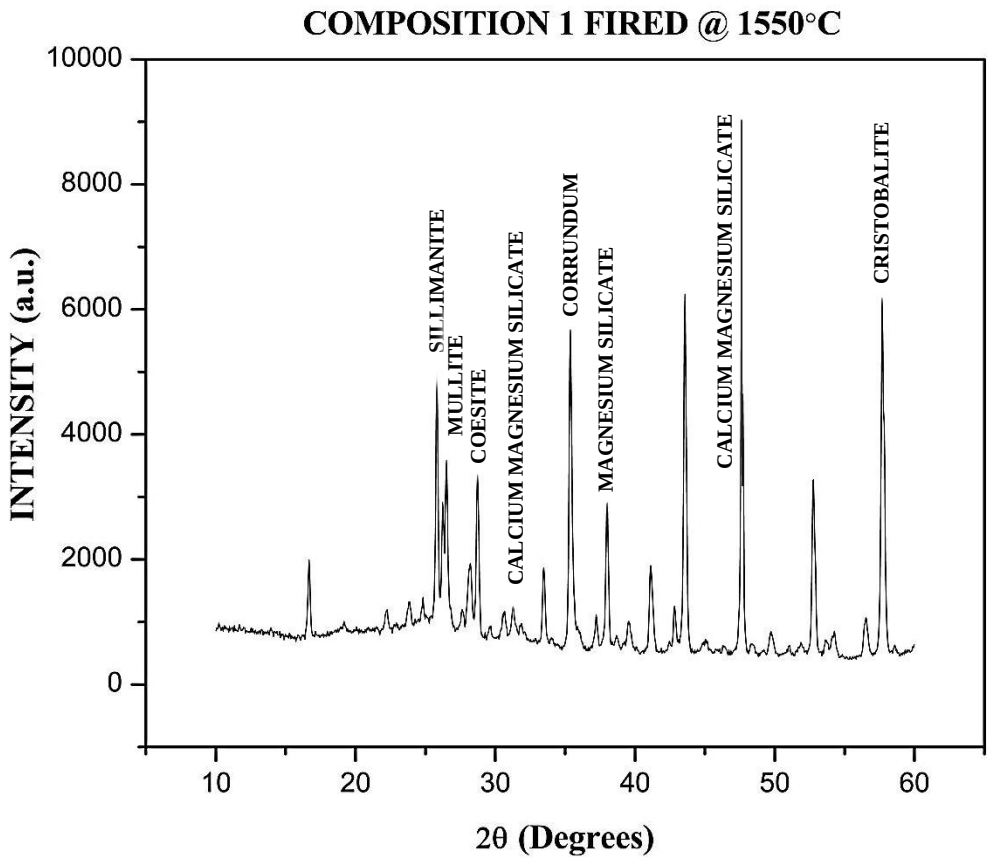

Fig 4.9 – Phase Analysis of glaze sample – composition 1 fired @ 1550°C/2hours

The Fig-4.9 shows the phase analysis of glaze composition 1 fired at 1550°C / 2 hours. The major phases found was Silica in the form of coesite, siliminite, cristobalite, alumina in the form of corundum, and some mullite phase was also seen to be formed. Apart from it magnesium silicate, calcium magnesium silicate was also found.

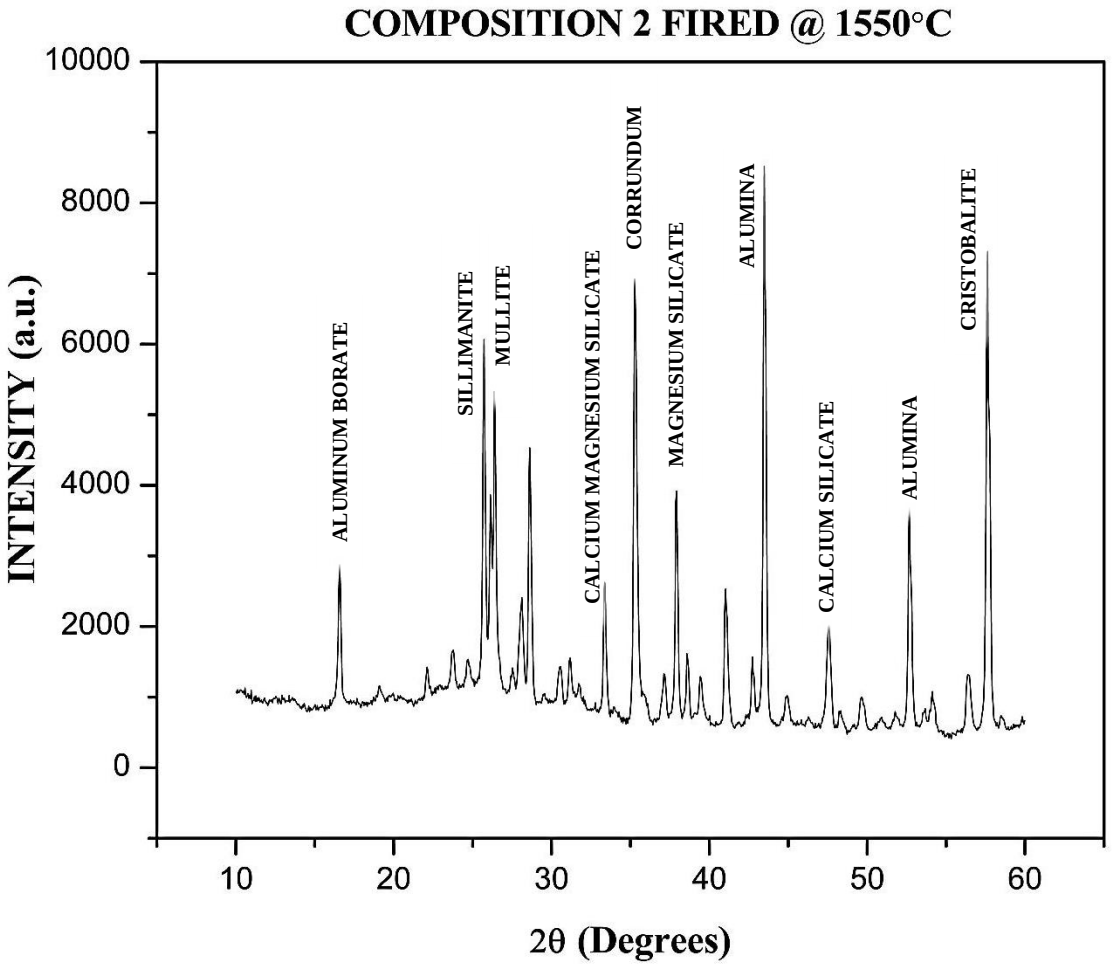

Fig 4.10 – Phase Analysis of glaze sample – composition 2 fired @ 1550°C/2hours

The Fig-4.10 shows the phase analysis of glaze composition 2 fired at 1550°C / 2 hours. The major phases were alumina, corundum, coesite, silimanite, calcium silicate, magnesium silicate, calcium magnesium silicate and mullite.

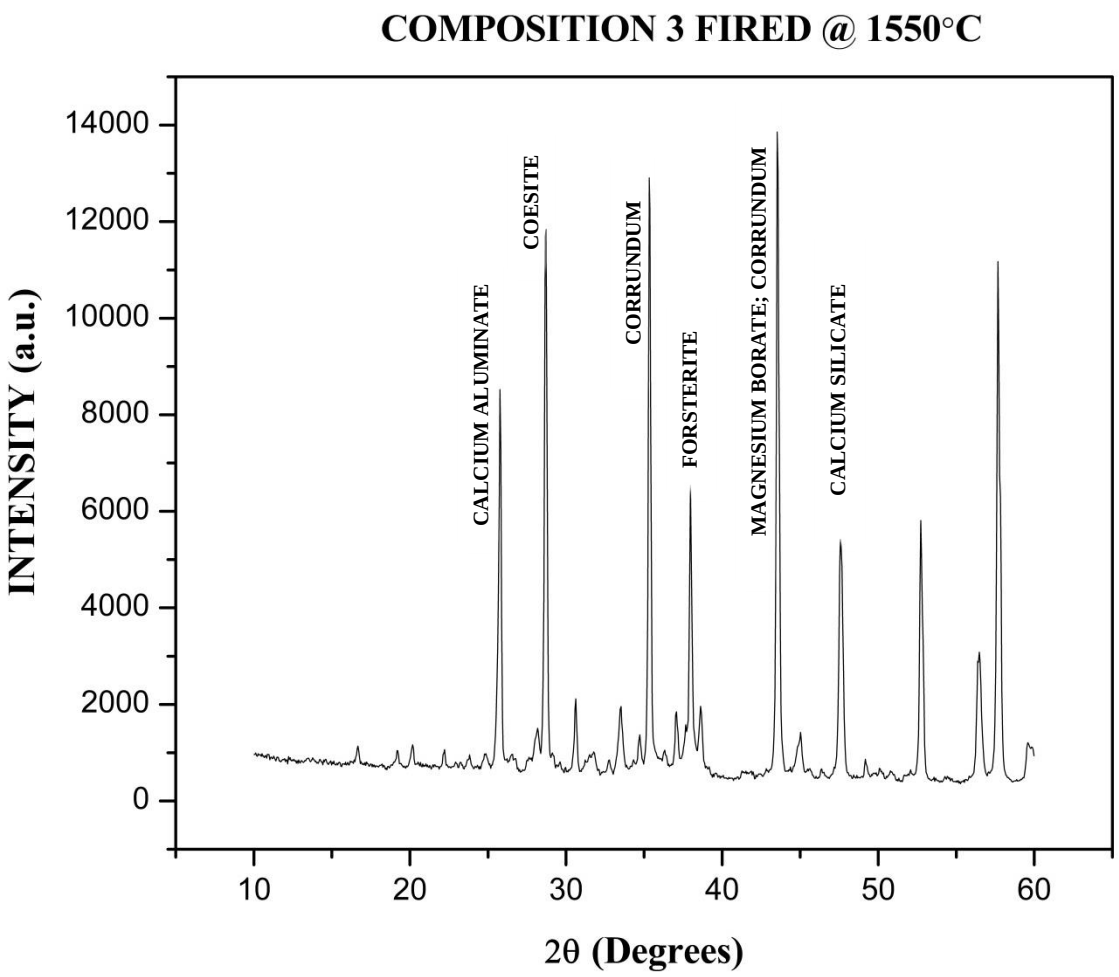

Fig 4.11 – Phase Analysis of glaze sample – composition 3 fired @ 1550°C/2hours

The Fig-4.11 shows the phase analysis of glaze composition 3 fired at 1550°C / 2 hours. The major phases formed were silica in the form of coesite, corundum, fosterite, calcium aluminate, alumina in corundum and calcium silicate.

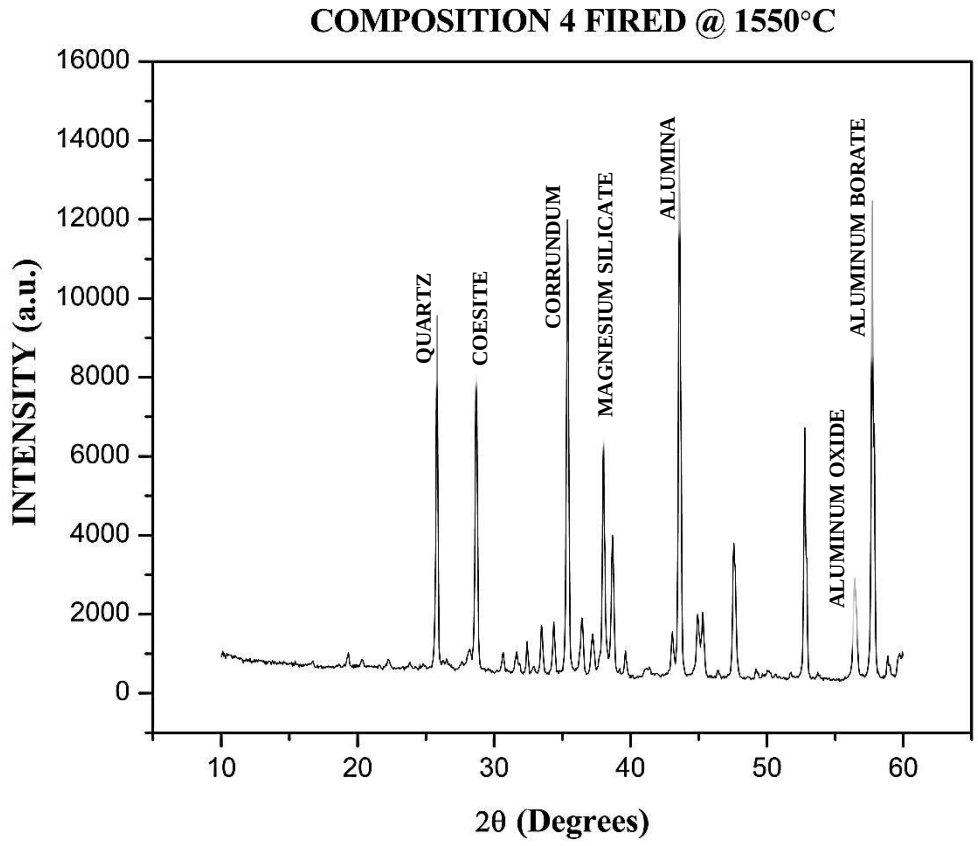

Fig 4.12 – Phase Analysis of glaze sample – composition 4 fired @ 1550°C/2hours

The Fig-4.12 shows the phase analysis of glaze composition 4 fired at 1550°C / 2 hours. The major phases present are silica in the form of Quartz and Coesite, Alumina, and alumina in the form of corundum, magnesium silicate and aluminum borate.

4.7 OXIDATION TEST RESULTS OF THE GLAZED ZIRCONIA GRAPHITE REFRACTORY

In this work, the glaze layer had been applied to the zirconia graphite refractory brick samples. Fig – 4.5 shows the surface of the unglazed and non-oxidized zirconia graphite refractory sample.

Fig – 4.13 Photographic image of unglazed and non-oxidized zirconia graphite refractory brick sample

In order to have a better comparative study, unglazed and oxidized zirconia graphite refractory had been shown in the fig 4.14.

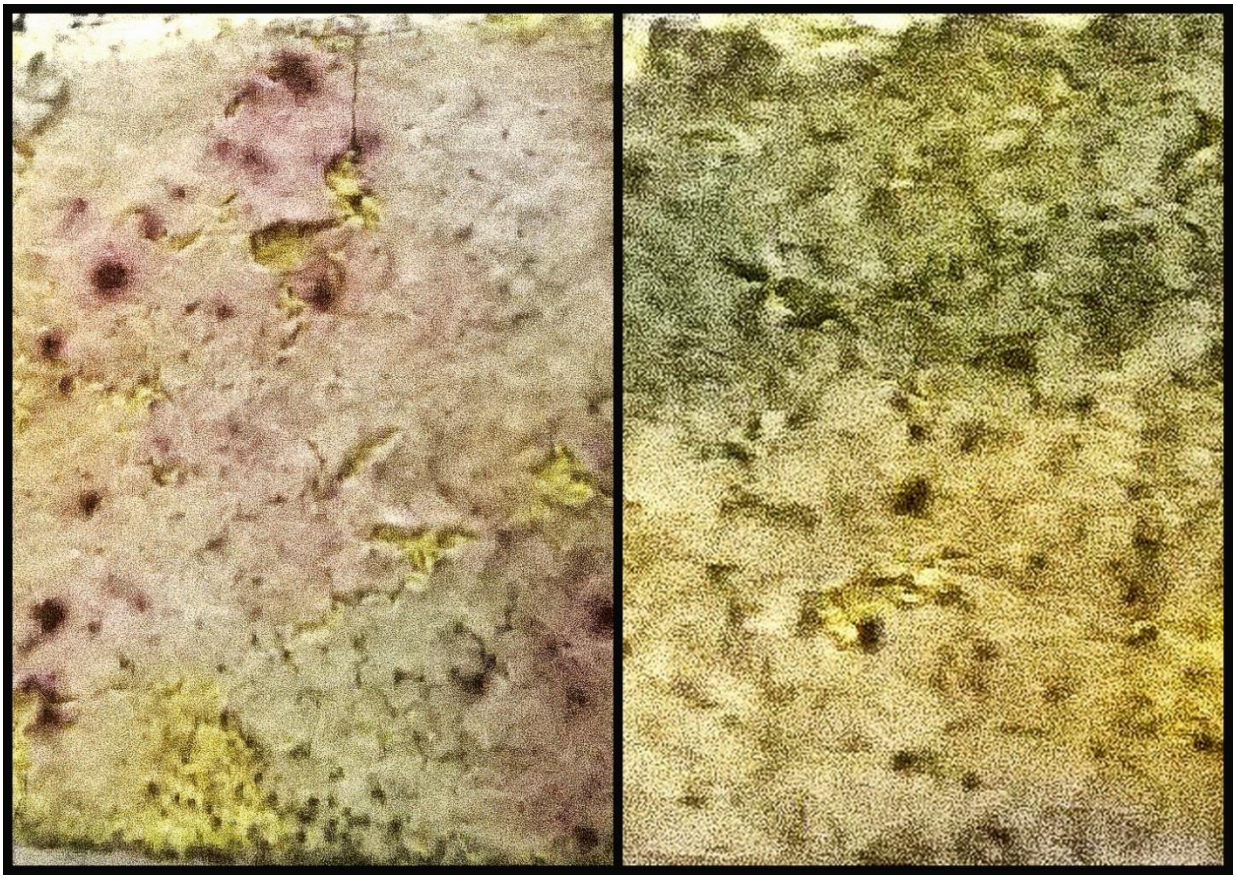

Fig - 4.14 Photographic image of the unglazed and oxidized zirconia graphite refractory brick sample at 1500°C and 1550°C

After glaze application, the brick samples had been subjected to oxidation at 1500°C and 1550°C. The fired glazed bricks had been cut in to slice, which had been shown in the Fig 4.15. It is should be noted that the interface between the glaze and the refractory brick had been clearly visible.

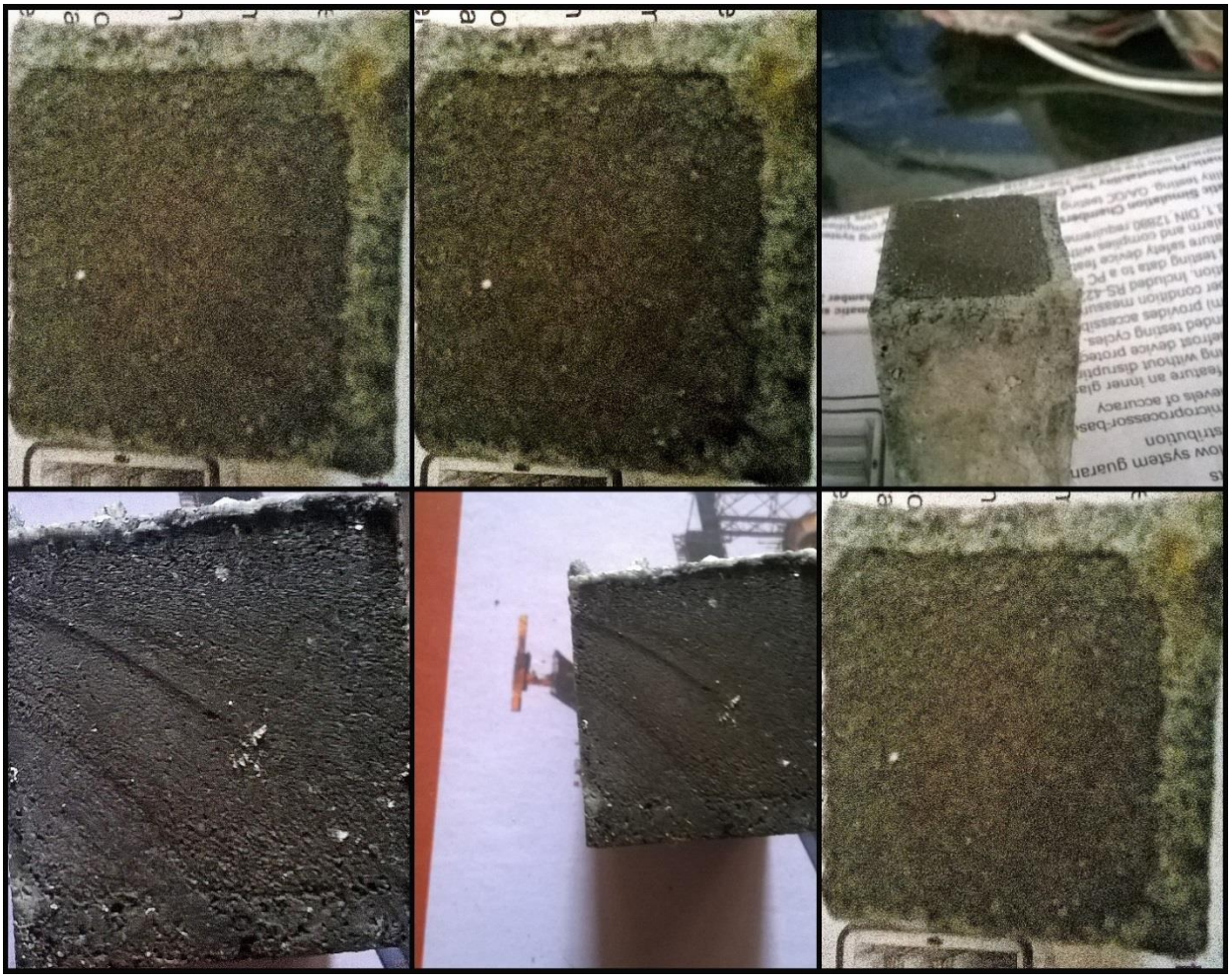

Fig 4.15 Photographic image of Glazed and oxidized zirconia graphite refractory brick samples

By viewing the photographic images given above, we can conclude that the level of oxidation of the glazed zirconia graphite bricks is comparatively less than the unglazed-oxidized zirconia graphite refractory bricks. This solves the purpose of utilizing the alkali free glaze layer on the carbonaceous refractory bricks.

CHAPTER 5

CONCLUSIONS, FUTURE WORK AND REFERENCES

5.1 CONCLUSIONS FROM THE RESULTS

1. An alkali free glass frits present in the glaze composition doesn't create any low melting phases on the glaze layer of zirconia graphite refractory bricks.
2. The level of oxidation in the glazed zirconia graphite refractory is comparatively less when compared with unglazed zirconia graphite refractory.
3. Most of the phases formed at the operating temperatures possess high melting point. Ultimately the viscosity retained in the glaze layer will be preferably high.
4. Thus the protective glaze layer created by the alkali free glass frits, along with the antioxidant restricts the level of oxidation, unless and until the glaze layer covers the entire surface of the refractory.

5.2 FUTURE WORK

1. Analysis of thermal shock resistance to the glazed zirconia graphite refractory bricks.
2. Experiments should be carried out for slag corrosion resistance for glazed zirconia graphite refractory.
3. Interfacial strength of the glaze and refractory lining has to be measured.

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